

EXAFS Characterization of Co-Mo Catalysts Used for the Production of Single-Walled Nanotubes

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Introduction: The fascinating properties of single-wall carbon nanotubes (SWNT) have opened a great number of potential applications for these unique materials. However, the high costs of the current production methods and the difficulty in making them available for large-scale manufacture have slowed down the process of bringing nanotube-based technologies to commercial practice. The catalytic decomposition of carbon-containing molecules such as CO is a potential method for large-scale production. We have investigated the synergism exhibited by Co and Mo in bimetallic catalysts, which result in a high selectivity towards the production of SWNT. The EXAFS and XANES characterization has allowed us to determine the state of Co and Mo before and after the production of SWNT, thus providing some insight into the mechanism of SWNT synthesis.

Methods and Materials: X-ray absorption data were obtained using beam line X-18B, equipped with a Si (111) crystal monochromator. The Co-Mo/silica samples were investigated as fresh samples after an initial treatment in H₂ (500°C)/ He (700°C) and as spent samples after different reaction periods for the production of carbon nanotubes. In both cases, they were not exposed to the air, but directly transferred from the reaction chamber to a He glove bag, where they were wrapped in Kapton tape and stored in He-purged sealed vessels. The EXAFS experiments were conducted in a stainless steel sample cell at liquid nitrogen temperature. The average spectrum was obtained by adding six scans. The pre-edge background was subtracted by using power series curves. The post-edge background was removed using a cubic spline routine. The spectra were normalized by dividing by the height of the absorption edge. To obtain structural parameters, theoretical references were obtained by using the FEFF and FEFFIT fitting programs from the University of Washington. In this routine, the Debye Waller factors for each bond type, the edge energy difference, the coordination number, and the difference in bond distances with respect to the theoretical reference, were used as fitting parameters.

Results: The XANES spectra of the K edge of Co ($E_0 = 7709$ eV) for the Co:Mo catalyst showed that after the pretreatment and before the reaction with CO, a significant fraction of Co is oxidized. However, as the reaction proceeds, metallic Co started to form and after 30 min the XANES was almost identical to that of a Co foil. The EXAFS data confirmed this conclusion. The structural analysis of the Co EXAFS data indicated that as the reaction preceded the Co reduction process was accompanied by an increase in metal particle size as indicated by the increase in Co-Co coordination number as a function of reaction time. The characterization of the state of Mo was conducted on the K edge of Mo ($E_0 = 20,000$ eV) both, on the fresh pretreated catalyst and after reaction. The XANES of the fresh Co:Mo catalyst pretreated at 700°C was similar, but not exactly identical to that of bulk MoO₃, which is the Mo species that one would expect if large Mo oxide aggregates were present. Supported Mo oxide can exhibit different structures and states of aggregation depending on the Mo loading, thermal treatment, and type of support investigated. Some features in the XANES spectra can be used to describe the state of Mo in the catalyst. For example, the pre-edge feature clearly observed for MoO₃ is due to a 1s-4d bound state transition, which is formally forbidden. However, it can become allowed by mixing of d-states with p-orbitals of the ligand. This mixing is very effective in compounds with tetrahedral geometry, and in those cases a strong pre-edge feature appears. When the geometry is octahedral, the transition is not allowed, but in MoO₃, the octahedral is distorted, and as a result, a small pre-edge feature is observed. In the fresh catalyst pretreated at 700 °C, the pre-edge feature was even smaller, indicating a less distorted octahedral configuration. The EXAFS data showed that the coordination of Mo in the fresh catalyst involves Mo-O bonds, but it is not the same as that of MoO₃ reference. At the same time, it does not exhibit coordination distances in the second shell region, which would indicate the presence of large aggregates. The results indicate that the fresh catalyst contains well-dispersed oxidized Mo species. These oxidized species may in fact be a combination of oxides and molybdates. Our own XPS data has shown that in the pretreated catalyst Mo is in a partially reduced state Mo(IV). After a 30-min reaction period, the near-edge spectrum of Mo showed a drastic change in appearance and became very similar to that of molybdenum carbide, Mo₂C. At the same time, the EXAFS exhibited peaks in the Fourier transform that exactly corresponded with those of the Mo₂C reference. The transformation of oxidized Mo species into Mo carbide during the reaction was indeed very clear, with only a small fraction of unconverted Mo remaining in the catalyst. This conversion was confirmed with the EXAFS data analysis. The best fit of the experimental data was obtained when the coordination sphere of the Mo was described as composed as Mo-C, Mo-Mo, and Mo-O. This indicates that the conversion to Mo carbide is not complete and a fraction of Mo remains as an oxidized species. In contrast to the Mo carbide formation observed in the bimetallic sample, the XANES spectra of a catalyst containing only Mo, without Co, did not exhibit after reaction a transformation into the carbide form. The shape of the near-edge for the spent Mo catalyst resembles that of the fresh Mo catalyst rather than that of the spent Mo:Co catalyst, which is clearly representative of Mo carbide. This result would indicate that, when Co is not present, the supported Mo oxide is not as easily converted into Mo carbide.